

## **Appendix H**

### **ISTD Reactivity: Differential Scanning Calorimetry**



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## Appendix H

### ISTD Reactivity: Differential Scanning Calorimetry

The reactivity studies for in situ thermal desorption (ISTD) were conducted in two laboratories and are presented in two parts:

- Appendix H—results of tests conducted at the Idaho National Laboratory Site using differential scanning calorimetry on nonradioactive isotopes
- Appendix J—results of tests conducted at Energetic Materials Research and Testing Center on drum-scale nitrate salt reactivity, where mixtures would undergo chemical reactions leading to innocuous products without explosions or runaway reactions.

The ISTD process is designed to destroy or remove organic material underground, particularly chlorinated solvents (Vinegar, Stegemeier, and Sheldon 1997). Most of the previous remediations using ISTD have been on contaminated soil sites, although one demonstration did include some debris (Shaw 1999). To use ISTD in the subsurface at the Radioactive Waste Management Complex would involve heating containerized waste, including chlorinated solvents, oils, and nitrate salts. During heating, these nitrate salts may melt and become potential oxidizers. No testing has addressed potential reactive interactions when slowly heating together containers of debris (Rocky Flats Plant [RFP] Series 743 and 744), organic sludge, and (RFP Series 745) nitrate salts. To address these potential issues, reactivity of selected mixtures of simulated waste using both bench-scale and drum-scale methods was tested. This section describes results of bench-scale instrumental thermal analysis using nitrate salt mixed with organic sludge surrogate or debris surrogate (carbon or wax) subjected to slow heating. See Appendix I for detailed description of drum-scale testing examining off-gas generation. See Appendix J for detailed description of drum-scale testing examining nitrate salt mixed with organic sludge surrogate, debris, and graphite subjected to ISTD well heating.

#### H-1. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN

The objectives are based on Yancey et al. (2003) for thermal analysis of a combination of RFP Series 745 “nitrate salt” and RFP Series 743 organic sludge, graphite, or debris that might be encountered during ISTD remediation of buried waste. The specific objectives are to:

- Determine if exothermic reactions might occur
- Determine temperatures of such reactions
- Estimate severity of reactions
- Determine if a reduced rate of heating changes the likelihood for reactions, their severity, and temperature of occurrence.

Previous instrumental thermal analyses used differential scanning calorimetry (DSC); some of these data (Heiser 1999) are used here for comparison purposes. The previous DSC work used surrogate and RFP nitrate salts, alone or in combination with machine oil (Texaco Regal Oil), polystyrene, polyethylene graphite, or cellulose (Heiser 1999). Although DSC was specified in Yancey et al. (2003), thermal gravimetric analysis (TGA) was used because the technique provides mass data in addition to the temperature data provided by DSC.

The current thermal effort addresses deficiencies in previous testing:

- Heating rate was too fast—10°C (18°F)/minute did not allow equilibrium to be reached before the temperature was again increased. The intrinsic reaction rate ( $k$ ) increases with temperature—according to the Arrhenius relation,  $k = A e^{-(E_a/RT)^a}$ —and the overall rate of the reaction (for reactions of first order or greater) increases with concentration,  $r = k f(C)$ . When the temperature is increased rapidly, more mass is available for reaction at a given  $k$ , leading to a faster reaction (or larger  $r$ ) than if a slower temperature increase is used, which allows more mass to be consumed at lower  $k$  values and leads to slower reactions throughout the heating process.
- Heating temperature limit was too low—Should go beyond 400°C (752°F) since reactivity was noted in large-scale testing between 400 and 500°C (752 and 932°F), and the heater temperature is expected to operate around 900°C (1,652°F). This leads to the possibility of a small proportion of the waste being exposed to that temperature.
- No mass data were obtained—Mass loss information helps interpret calorimetry data.

The past thermal analysis heating rate of 10°C (18°F)/minute was lowered as far as the thermal analysis instrument would allow to 0.1°C (0.18°F)/minute. This is still faster than the ISTD heating rate for any substantial quantity of material in the field. Field ISTD operations heated wet soil to dryness at the rate of 0.001°C (0.0018°F)/minute (about 85°C [185°F] in 2 months). Once the soil is dry, the heating rate is much faster close to 0.005°C (0.009°F)/minute (about 220°C [428°F] in 1 month) (Shaw 1999). This heating rate is critical in determining reactivity. Instrumental calorimetry uses a small sample size. Small particle size within the mixture can also be a factor in that the surface-area-to-volume ratio may be smaller than that in waste. The small sample size and induction period were addressed in the larger-scale reactivity test.

Most of the instrumental thermal analyses proposed in Yancey et al. (2003) using organic sludge and nitrate salts, including instrument calibration, were run before the 10-year-old thermal analysis instrument irreparably failed. Thermal analysis of surrogate waste salts and organic sludge, both alone and combined at slow heating rates, was performed.

## H-2. EXPERIMENTAL DESIGN AND PROCEDURES

Instrumental thermal analyses (such as DSC and TGA) are analytical techniques that characterize specific heat, enthalpies of transition, reactivity, temperature of reaction, and magnitude of reaction during heating. Instrumental thermal analyses are small-scale measurements (0.02 to 0.1 g [0.0007 to 0.004 oz]) using a bench-top laboratory instrument. The result is a graphical output of exotherms (heat given off, positive heat flows on the graphs) and endotherms (heat absorbed, negative heat flows on the graphs) (i.e., heat given off or heat absorbed versus system temperature).

Thermal instrumental analysis techniques measure sample temperature changes relative to a reference material. Sample and reference substances are heated in separate holders. Averaging temperature circuits control temperatures of the two materials to match a predetermined temperature ramp (programmed time-temperature). A differential temperature circuit measures the small differences between the sample and reference holders and proportions the power to each holder to keep the temperatures equivalent. The difference in power is proportional to the heat absorbed or evolved by the

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a. Where “A” is a constant, “E<sub>a</sub>” is the activation energy, “R” is the ideal gas constant, and “T” is the temperature in absolute units.

sample (e.g., during transitions such as melting, crystal phase changes, and endothermic or exothermic reactions).

The electrical energy required to maintain both materials at the same temperature is recorded on the left side of the y-axis of each scan versus temperature rise on the x-axis. A negative peak occurs when more heat is absorbed (more outside electrical energy required to maintain temperature) in the test sample than in the reference sample, thus indicating an endothermic reaction in the sample. Endotherms are typically from physical changes such as melting, phase transition, and vaporization and from chemical changes such as pyrolysis and some decomposition. A positive peak indicates an exothermic reaction: heat is given off (less outside electrical energy required to maintain temperature) from the test sample. Exothermic reactions include chemical reactions such as combustion (e.g., oxidation of carbon present) and some decomposition. If the unknown sample gives off more heat than the reference, an exotherm is recorded.

The difference in heat from the sample and the reference empty cup is constantly measured and displayed on a graph with the loss in weight as heating progresses. Heat is absorbed in the case of endothermic-nitrate decomposition, or organic pyrolysis, or given off in the case of exothermic-organic oxidation. This heat is compared to the cup containing no sample or a reference sample and graphed as the temperature is increased at a set rate. The reference material for each run was an identically prepared empty alumina pan.

The DSC provides good thermal resolution but lacks the ability to obtain weight data as the heating progresses. The TGA is similar in calorimetry operation to DSC but, in addition, provides weight loss data while the heating takes place. The sample cup is on a microbalance, which records weight data while calorimetry takes place. Basically, the calorimetry technique of DSC is added to one that additionally gives weight loss data as the sample is heated.

Thermal analysis outputs are time, temperature, and energy absorbed or released as the sample heats. In the case of TGA, weight loss also is plotted as percent of total weight along the right side of the y-axis. The temperatures are measured to  $\pm 0.5^{\circ}\text{C}$  ( $32.9^{\circ}\text{F}$ ) as the reference is raised from  $20^{\circ}\text{C}$  ( $36^{\circ}\text{F}$ )/minute to as low as  $0.1^{\circ}\text{C}$  ( $0.18^{\circ}\text{F}$ )/minute, from 25 to  $900^{\circ}\text{C}$  ( $77$  to  $1,652^{\circ}\text{F}$ ). Fast heat rates gave better sensitivity on the fine details and are typically the way DSC is run, but fast heat rates do not simulate the extremely slow heating rate of ISTD of  $300^{\circ}\text{C}$  ( $572^{\circ}\text{F}$ )/month or  $0.007^{\circ}\text{C}$  ( $0.013^{\circ}\text{F}$ )/minute.

Weights may change with heat-induced chemical reactions (e.g., combustion and decomposition) and physical changes (e.g., vaporization), but do not change with thermal changes such as melting or transitional shifts. This allows both exotherms and endotherms to be better identified. Most exotherms result in mass loss. The temperature and rate of this mass loss help indicate the difference between reactions of vaporization and oxidation or combustion.

Instrumental thermal analysis techniques heat between 10 and 20 mg (0.0004 and 0.0007 oz) of sample in a small 6-mm-diameter (0.2-in.-diameter) pan, boat, or cup. Past samples were run in metals: platinum, gold, or aluminum; the present set of experiments used alumina ceramic. Platinum and gold were not available, and aluminum reacts with the nitrate salts when they melt. Alumina ceramic also can react with nitrate salts, but the reaction generally starts at temperatures of  $850^{\circ}\text{C}$  ( $1,562^{\circ}\text{F}$ ) or higher.

Past thermal instrumental analyses used DSC in the absence of air, both in sealed and in open cups with nitrogen purge gas flowing through the chamber. The present analyses were run with an air purge flowing at approximately 20 mL/minute in open cups. This provides realism as ISTD occurs with some amount of air in an atmospheric pressure (slight vacuum) configuration.

Additional thermal instrumental analyses used TGA on nitrate salts to assess interactions between the waste salts and carbon containing waste surrogates of organic sludge and debris as they are slowly heated. The TGA provided weight data in addition to the calorimetry data. Samples were heated to the heater temperatures of 900°C (1,652°F).

The basic experimental sequence for all reactivity testing, including instrumental thermal analysis, is:

1. Prepare waste and contaminant surrogates
2. Place samples in heating chamber and slowly heat samples
3. Record reaction heat and weight loss and qualitative changes.

Testing was in general accordance with ASTM E537-02, “Standard Test Method for the Thermal Stability of Chemicals by Differential Scanning Calorimetry.”

The following waste simulants were prepared and tested both individually and in potentially reactive mixtures, as listed below:

- Single waste surrogates:
  - Nitrate salt sludge components: sodium nitrate and potassium nitrate.
  - Nitrate salt sludge surrogate composed predominantly of sodium nitrate and potassium nitrate. The complete recipe is provided in Table A-2 in Appendix A.
  - Organic sludge surrogate containing Texaco Regal Oil, calcium silicate, and chlorinated solvents. The complete recipe is provided in Table A-3 of Appendix A.
- Surrogate mixes:
  - Nitrate salt sludge surrogate plus carbon powder, organic sludge surrogate, or wax.

The mixes of salt with these carbon sources were first prepared in a macroamount (~10 g [0.4 oz]). Salt organic mixtures were prepared by weighing out gram quantities of the salt and organic sludge, carbon powder, or wax into a clean and dry vial, extensively mixed both with a spatula and shaken vigorously until homogenous. A subsample was weighed and added to the alumina boat for calorimetry analysis.

Three waste surrogates containing carbon were chosen that could be mixed on a very small scale and simulate prevalent waste types containing carbon that might be encountered in RFP waste. There is some graphite in the waste from graphite molds, and reactivity of this has been extensively studied (Dick 2001); however, graphite is a small portion (<0.2%) of the material containing carbon. Most of the drummed waste containing carbon is combustible trash (e.g., cardboard, plastic, or paper) or organic sludge (Clements and Kudera 1985). When heated, the combustibles will char, forming some form of carbon. Carbon powder is a good surrogate for this and far more reactive than graphite.

Debris contains a significant portion of plastic. Plastic is aliphatic carbon and hydrogen and is well simulated by wax. Wax is also the base ingredient of one of the grouts for the in situ grouting portion of this project, and its reactivity with salts was of interest if the wax was used as a solidification agent. Wax and plastic thermal analysis has been performed previously, but not using a slow heating ramp.

Organic sludge surrogate was used directly and also has been reactivity tested before both by thermo analysis (Heiser 1999) and macrotesting (Dick 2001). The three waste surrogates containing

carbon provide a range of reactivity potential with nitrate salts covering the probable organic waste that could be in proximity with nitrate salts. The results of previous testing indicate that carbon powder, representing char from pyrolyzed debris, is the most reactive. The organic sludge is the least reactive; it is essentially inert with respect to specific nitrate salt interactions.

All the organic sludges and nitrate salts were disposed of in drums. Evidence from the Glovebox Excavator Method Project retrieval showed that while most of the drums have completely disintegrated, many of the plastic bag liners are still intact, especially toward the top of the waste seam. The Glovebox Excavator Method Project retrieval also showed that a substantial amount of soil is present within the waste seam (DOE-ID 2004).

Tests were run to 900°C (1,652°F) at a heating rate of 10°C (18°F)/minute, 1°C (1.8°F)/minute, 0.5°C (0.9°F)/minute, and 0.1°C (0.18°F)/minute (see Table H-1 for details). All are heat rates faster than the typical field rate of 0.01–0.005°C (0.018–0.009°F)/minute because of the limits of the instrument. Replicates were run on the single ingredients and several of the mixes.

Table H-1. Thermal analysis summary.

Sample	Heating Rate				Purpose
	(10°C/minute)	(1°C/minute)	(0.5°C/minute)	(0.1°C/minute)	
Purpose of heating rate	Standard instrument heating rate	ISTD heater area	ISTD heater well area	ISTD soil heating slowest instrument heating rate	—
Potassium nitrate	No reaction	No reaction	N/A	N/A	Calibration and quality assurance
Sodium nitrate	No reaction	No reaction	N/A	N/A	Calibration and quality assurance
Salt surrogate mixture: 60% sodium nitrate, 30% potassium nitrate, 10% soluble salts	No reaction	No reaction	N/A	N/A	Baseline and operational assessment
Organic sludge chlorinated solvents, oil, and solid absorbent	No reaction	No reaction	N/A	N/A	Baseline and operational assessment
54% salt + 46% organic sludge	N/A	No reaction	N/A	N/A	Operational assessment
55% salt - 45% carbon powder (carbon excess)	N/A	Reaction	N/A	N/A	Safety assessment
83% salt - 17% carbon powder (optimum ratio)	Reaction	Reaction	Slight reaction	No reaction	Safety assessment
40% salt + 60% wax	Reaction	Reaction	N/A	No reaction	Safety assessment

ISTD = in situ thermal desorption

### H-3. EQUIPMENT AND MATERIALS

The current scans were run on a rheometer TGA with alumina pans. Some runs did not give complete weight data as the gravimetry balance started to malfunction on the only instrument available during the test period. Three carbon sources were mixed with nitrate salts: organic sludge, carbon powder, and wax. Waste surrogate materials were reagent-grade chemicals for salts, carbon powder, and solvents and commercial grade for absorbents, oil, and paraffin. The nitrate salt and organic sludge surrogates were prepared according to recipes in Appendix A.

### H-4. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION

The TGA temperature ramp rate was verified for both accuracy and stability in the slow heating rate mode. The sample boat temperature was ramped from 25 to 900°C (77 to 1,652°F) at 0.5°C (0.9°F)/minute. A temperature-versus-time graph of 0.5°C (0.9°F)/minute heat rate in the range of interest from 300 to 700°C (572 to 1,292°F) is shown in Figure H-1. The setting of 0.5°C (0.9°F)/minute was actually 0.49°C (0.88°F)  $\pm$  0.004°C (0.007°F)/minute within the instrument stability specification of 1% and rate accuracy of 2%. Fast heat rates, 10 or 20°C (18 to 36°F)/minute, gave better sensitivity on the fine details and are routinely used in both DSC and TGA thermal analysis; however, this heat rate does not simulate the extremely slow heating rate of ISTD at most temperatures of 300°C (540°F)/month or 0.007°C (0.013°F)/minute.

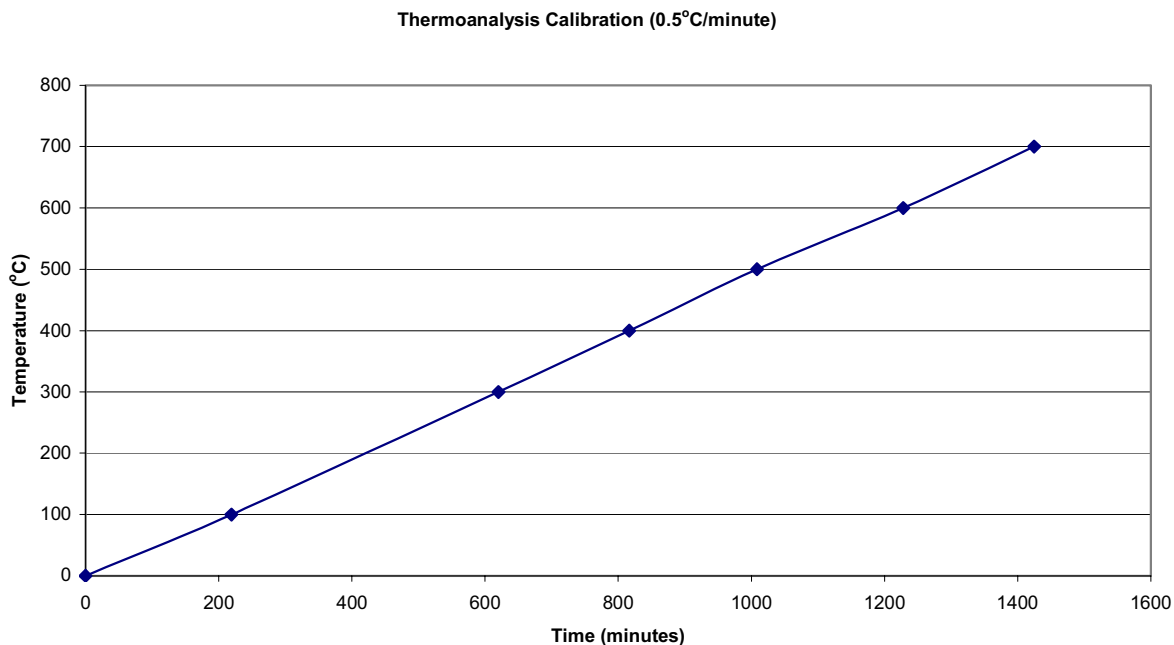


Figure H-1. Thermal analysis calibration (0.5°C [0.9°F]/minute).

### H-5. RESULTS AND CONCLUSIONS

The reaction between sodium nitrate and pure carbon proceeds according to one or more of the equations presented in Table H-2. The more complete the combustion to carbon dioxide and nitrogen, the more energy is released. Nitrate organic reaction ratios vary, but the stoichiometric ratio of nitrate to carbon, 85-to-15, can yield complete reduction to nitrogen gas and, thus, is the most exothermic of the reactions.

Carbon is one of several elements (iron, nickel, and copper can also reduce nitrate salts) that can result in exothermic nitrate salt reactions. While iron, nickel, and copper are present in the waste contained in the Subsurface Disposal Area, they are not expected to be generally present in a high surface area or finely divided form. Carbon is expected to be present in a wide variety of forms (e.g., paper, filters, organic chemicals, plastic, and graphite), many of which have high surface areas or are in a finely divided form. For this reason, only carbon was studied in these experiments.

The absence of a reductant (carbon) in the decomposition upon heating nitrate salts leads to an endothermic reaction like melting and requires a high temperature and a continual input of heat. This is why the nitrate salts will not readily decompose without carbon (or another reducer) present.

The exact reaction products depend on several factors, including the carbon available, the induction period, the contact between materials, the contact time, and the physical forms of the reactants. The physical forms of reactants are the most critical parameter for inducing excessive reactivity and are not shown in chemical equations. In all our instrumental tests, the reactions of molten salts occur well above the salts' melting point.

The nitrate salts contain less than 90% alkali oxidizers (the alkali oxidizers are the reactive portion of the salts, sodium and potassium nitrate, with the remaining salts, alkali chlorides, sulfates, bicarbonates, and fluorides) (Shaw, Anderson, and Davis 1993). Thus, to achieve a stoichiometric nitrate-carbon equivalent (e.g., the optimum 85-15) ratio and assuming a pure carbon source, an 88-12 ratio of nitrate salt surrogate-to-carbon is needed. The organic sludge surrogate is not a pure carbon source (such as that provided by charred debris, charcoal, carbon black, or graphite) but contains a paraffinic oil and chlorinated hydrocarbons, of which 86% is carbon. The paper and cardboard portion of combustible debris before charring can be approximated by cellulose, which is 48% carbon. The carbon in the paper and cardboard was observed to be generally more reactive than the carbon in the organic sludge surrogate with nitrate salts. This may be because of the combination of oxygen and hydrogen present in the cellulose-based materials, while only hydrogen is present in the hydrocarbon-based materials tested.

Table H-2. Nitrate and carbon reactions in order of increasing weight loss.

Chemical Reaction	Nitrate Salt Carbon Mass Ratio (wt:wt)	Theoretical Decomposition Weight Loss in Salt Surrogate (wt%)	Heat of Reaction (calories/mole)
$4\text{NaNO}_3 + 5\text{C} \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{CO}_2 + 2\text{N}_2$	85:15	32	1,570
$2\text{NaNO}_3 + \text{C} \rightarrow \text{Na}_2\text{CO}_3 + \text{NO} + \text{NO}_2$	93:7	32	70
$6\text{NaNO}_3 + 8\text{C} \rightarrow 2\text{Na}_2\text{O} + \text{Na}_2\text{CO}_3 + 7\text{CO} + 6\text{NO}$	84:16	47	-623 <sup>a</sup>
$4\text{NaNO}_3 + 4\text{C} \rightarrow 2\text{Na}_2\text{O} + 3\text{CO} + 3\text{NO} + \text{NO}_2 + \text{CO}_2$	88:12	54	-232 <sup>a</sup>
$2\text{NaNO}_3 \rightarrow \text{Na}_2\text{O}_2 + 2\text{NO}_2$	No carbon	46	-491 <sup>a</sup>

a. Negative heat of reaction is endothermic, requiring heat.

C = carbon	Fe <sub>2</sub> O <sub>3</sub> = iron oxide	Na <sub>2</sub> O <sub>2</sub> = sodium peroxide
CO = carbon monoxide	N <sub>2</sub> = nitrogen	NO = nitrous oxide
CO <sub>2</sub> = carbon dioxide	NaNO <sub>3</sub> = sodium nitrate	NO <sub>2</sub> = nitrite
Fe = iron	Na <sub>2</sub> CO <sub>3</sub> = sodium carbonate	O <sub>2</sub> = oxygen
	Na <sub>2</sub> O = sodium mono-oxide	

Temperature accuracy for TGA and DSC measured values is compared with standard values and listed in Table H-3. Good agreement for both techniques is shown for the melting points of potassium nitrate and sodium nitrate. The relative percent error for melting points of both sodium nitrate and potassium nitrate is less than 1%. Table H-4 also gives melting and boiling points for selected organic

compounds that might be present in the organic sludge surrogate or plastic debris as they are heated. Instrumental analysis agreement is good for the eutectic melting temperature of the salt surrogate and the boiling point of the Texaco Regal Oil. The TGA and DSC scans also agree well with each other, though there are more features in the DSC scans.

Table H-3. Thermal properties of Rocky Flats Plant waste components.<sup>a</sup>

Property	Literature Value		Thermal Gravimetric Analysis Value (°C)	Differential Scanning Calorimetry Value (°C)	Waste Stream
	(°C)	(°F)			
Water BP	94	201	—	—	Nitrate salt sludge surrogate, inorganic sludge surrogate
Nitrate salt eutectic low	—	—	213	212	Nitrate salt sludge surrogate
Nitrate Salt eutectic low with Texaco Regal Oil	—	—	220	218	Nitrate salt sludge surrogate
Nitrate salt eutectic average	—	—	218	220	Nitrate salt sludge surrogate
Nitrate salt eutectic high	—	—	223	240	Nitrate salt sludge surrogate
Sodium nitrate MP	308	586	307	307	Nitrate salt sludge surrogate
Potassium nitrate MP	334	590	332	—	Nitrate salt sludge surrogate
Low reactive temperature debris and salt	—	—	309	316	Debris
Texaco Regal Oil BP	361	681	360	370	Organic sludge surrogate

a. Heiser 1999; Reid, Prausnitz, and Poling 1987; Shaw 1999

BP = boiling point (at 680 mm)

CRC 2000

MP = melting point

Table H-4. Thermal properties of Rocky Flats Plant waste components.

Property	Literature Value		Waste Stream Origin
	(°C)	(°F)	
Trichloroethane boiling point	70	157	Organic sludge
Carbon tetrachloride boiling point	72	162	Organic sludge
Trichloroethylene boiling point	83	182	Organic sludge
Perchloroethylene boiling point	—	—	Organic sludge
Tar softening point	96	205	Plastic in debris
C <sub>10</sub> H <sub>8</sub> naphthalene (2% of coal tar)	218	424	Plastic in debris
C <sub>11</sub> H <sub>10</sub> (1% of coal tar)	241	466	Plastic in debris
Tar flash point low	274	525	Plastic in debris
Tar flash point high	316	600	Plastic in debris
C <sub>14</sub> H <sub>10</sub> anthracenes (1% of coal tar)	340	644	Plastic in debris

The experimental thermal analysis, current TGA, and past DSC results are shown graphically for single waste surrogates and for combinations of surrogates in the discussion that follows.

## H-5.1 Single Waste Stream Thermo Analysis Results

Thermal analysis of the organic sludge and nitrate salt surrogates was performed individually before they were run as mixtures. Data from these single waste surrogates are listed in Table H-5. Thermal analysis of oil, sodium nitrate, and potassium nitrate (the base ingredients of the waste surrogates) was run to:

- Compare instrumental thermal analysis techniques TGA and DSC
- Baseline the physical characteristics
  - Melting point of salts
  - Boiling point of salts and organics
  - Vaporization rate of organics in sludges
  - Salt decomposition rate.

The melting point for the primary alkali nitrate components of the salt simulant and the boiling point for the oil in the organic sludge match the literature values listed (see Table H-4) for these chemicals verifying adequate calibration of the instrument. Table H-5 lists thermal analysis results for both waste components and waste simulants with literature values for physical constants of organic sludge breakdown products of interest to help interpret the thermal analysis results. Table H-7 lists the actual weight changes observed during heating. The thermal analysis results for single waste components are discussed first, followed by waste simulant mixtures of organics with the nitrate salts. Finally, the relationship of instrumental analysis results to drum-scale tests and ISTD applications is summarized.

Table H-5. Thermo gravimetric analysis summary of individual waste surrogates.

Mixtures	Reactive Range Peak (°C)		Maximum Weight Loss Temperature Range (°C)		450°C Cumulative Weight Loss (wt%)	Weight Loss Peak (wt%)	Exotherm Peak (°C)	Melting Point (°C)	Duration Peak (minutes)	Ramp Rate (°C/minute)	Maximum Temperature (°C)	Net Peak (mW)
	Start	Finish	Start	Finish								
Organic sludge 1	360	550	50	300	54	7 <sup>a</sup>	475 <sup>a</sup>	—	190 <sup>a</sup>	1	900	1 <sup>a</sup>
Organic sludge 2 <sup>a</sup>	360	545	50	300	53	9 <sup>a</sup>	460 <sup>a</sup>	—	185 <sup>a</sup>	1	900	1.2 <sup>a</sup>
Salt mixture	350	370	550	750	3	<1	360	212	20	1	900	2
Salt mixture	390	440	650	850	2	<1	417	214	5	10	1,200	1.7
Potassium nitrate	—	—	600	800	0.6	—	—	332	—	10	1,200	-8.7 <sup>b</sup>
Potassium nitrate	—	—	0	500	6	—	—	332	—	1	500	-0.4 <sup>b</sup>
Sodium nitrate	—	—	620	820	0.2	—	—	310	—	10	1,200	-47 <sup>b</sup>
Sodium nitrate	—	—	500	720	0.4	—	—	304	—	1	800	-7.7 <sup>b</sup>

a. The organic sludge peak was selected as a broad area of greatest combustion  
b. These are endotherms for nitrate salt components.

### H-5.1.1 Nitrate Salt Surrogate

The thermal analysis of the nitrate salts from DSC in Figure H-2 (Heiser 1999) and TGA in Figure H-3—though different in general appearance, scale, and baseline—shows similar inflection points, particularly the lowered eutectic melting point for the salt mixture.

The graphical results of DSC thermal analysis for the RFP nitrate salt sludge waste tested at Brookhaven National Laboratory for the *Thermal Analysis of INEEL Pad-A Salt Waste Using Differential Scanning Calorimetry* (Heiser 1999) are depicted in Figure H-2. The results of the TGA run on nitrate salt sludge surrogate are depicted in Figure H-3. Minor differences appear between the two figures; this is expected since the nitrate sludge and the surrogate nitrate sludge are similar but not identical in composition.

Peaks occur at the expected locations for the surrogates and salts. Minor peaks (such as the loss of waters of hydration and phase transition of the salts as they heat) are apparent depending on resolution, which is a function of the instrument but also the heating rate. Both the TGA and DSC calorimetry scan show the endothermic reduced melting range of 210 to 240°C (410 to 464°F), which is near the literature value for the melting point for the eutectic 212°C (413.6°F) mp when sodium nitrate (308°C [586.4°F] mp) and potassium nitrate are mixed (334°C [633.2°F] mp) as listed in Table H-2.

Three major endothermic features are noted. Below 100°C (212°F), the DSC has two peaks and the TGA one peak that correspond to the loss of water hydration. Following this, both plots show the transition peak for potassium nitrate (131°C [267.8°F]) and the composite eutectic melting point (210 to 240°C [410 to 464°F]) for sodium and potassium nitrates.

For both salt samples, a minor peak is seen in the thermo analysis around 380 to 420°C (716 to 788°F), which is apparently a reaction of the salts with the 1% organic (see Table A-2 of Appendix A) expected to be present in the nitrate salt waste and added in the form of EDTA to the nitrate salt surrogate.

The nitrate salt surrogate sample was heated to higher temperatures than the nitrate salt waste sample; the waste would be expected to behave similarly to the surrogate. Heating salt surrogate alone well past the eutectic melting point of 210 to 240°C (410 to 464°F) and beyond the reported decomposition temperature (380°C [716°F]) is required to eventually decompose nitrates (CRC 2000). According to the TGA weight curve, this occurs at 500 to 650°C (932 to 1,202°F). This was verified by furnace tests and postheating nitrate salt analysis (see leach test results), indicating loss of weight was nitrogen oxide gases (brown and white gas observed) from the sodium nitrate and potassium nitrate. Additionally, vaporization of the remaining sodium and potassium oxides will occur at these temperatures. The TGA and furnace tests indicate the nitrates of the salts have been vaporized before 700°C (1,292°F) and all of the organics in sludge are removed or have been charred by 300°C (572°F).

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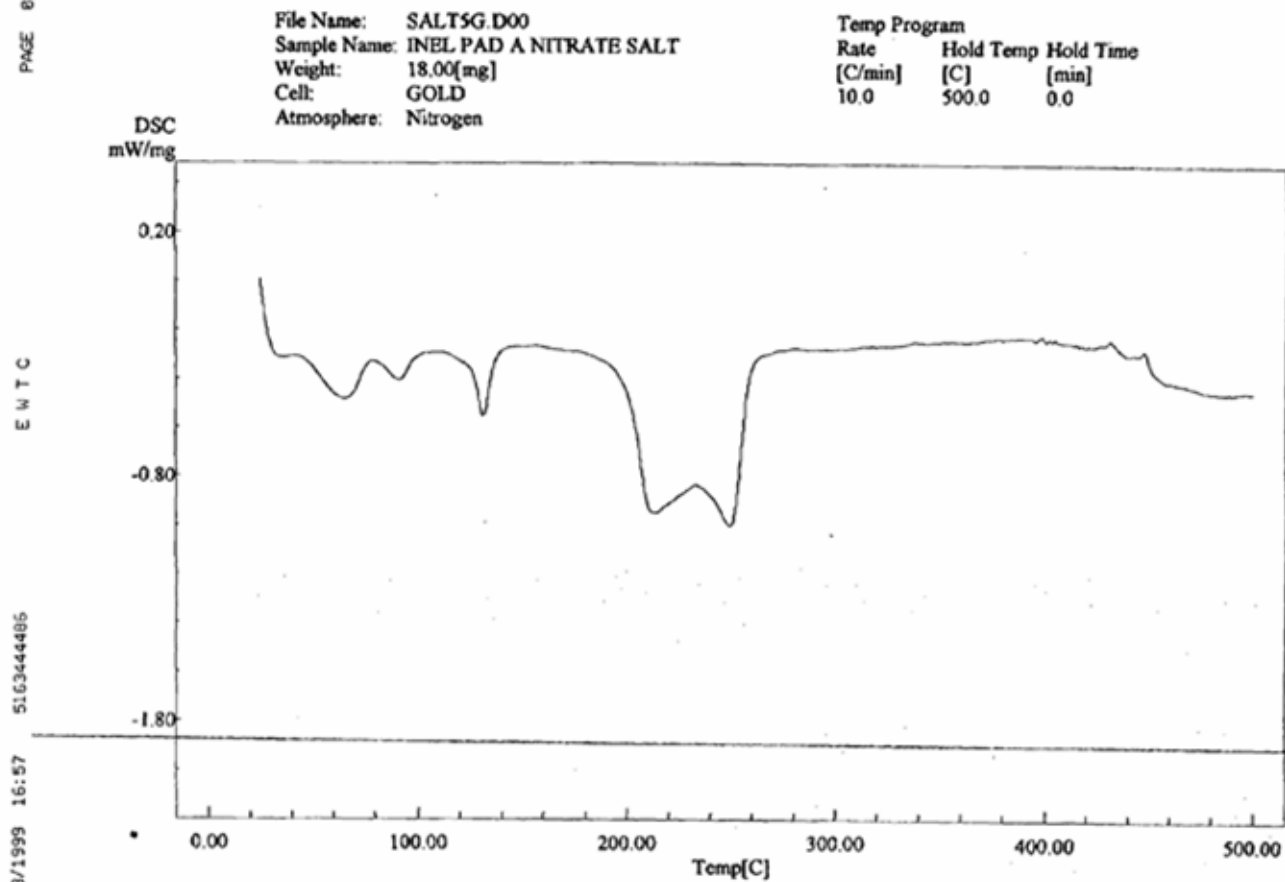


Figure H-2. Differential scanning calorimetry of nitrate salt waste.

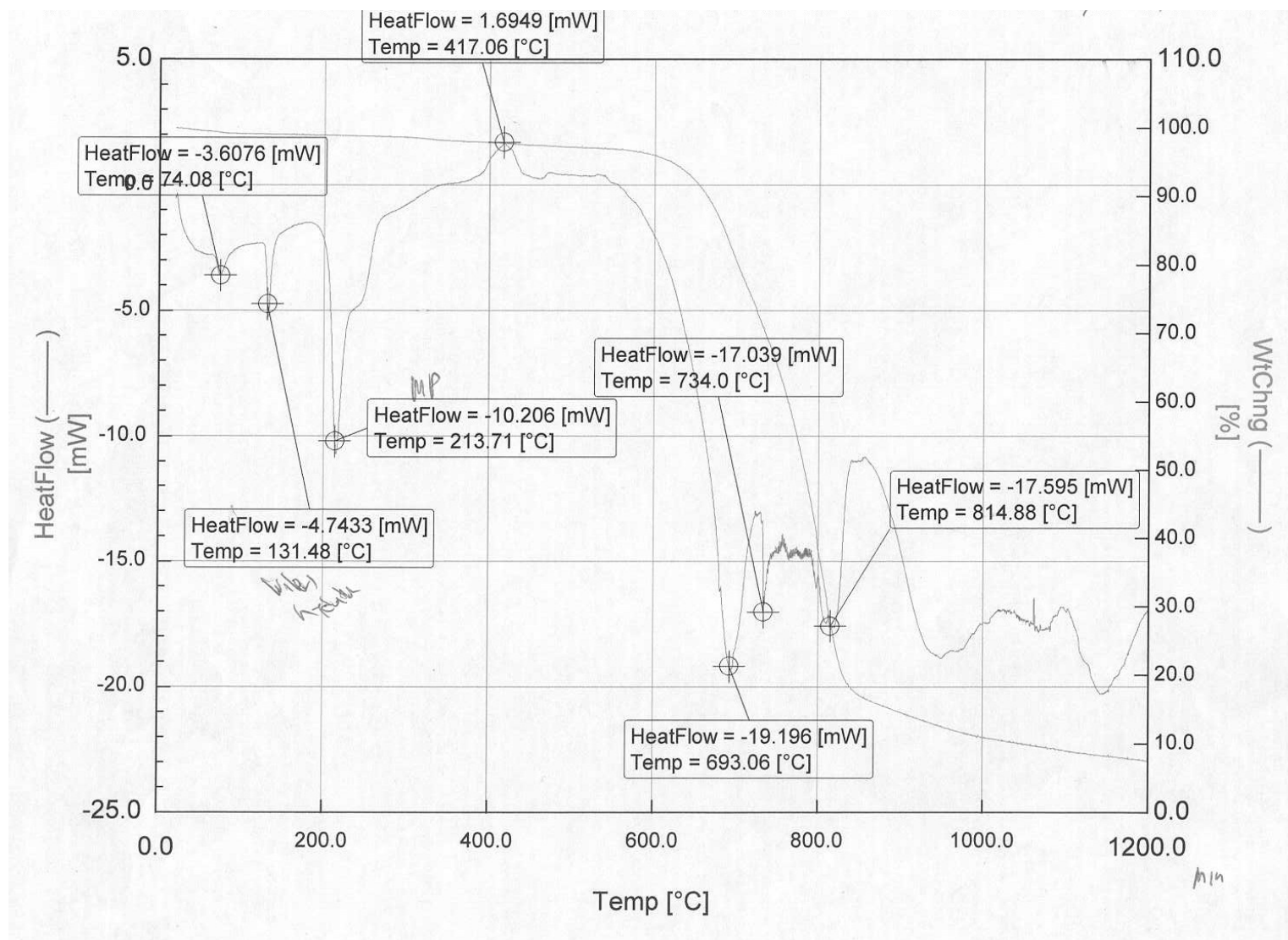


Figure H-3. Thermal gravimetric analysis of nitrate salt surrogate run at 10°C (18°F)/minute.

### H-5.1.2 Organic Sludge Surrogate

The results of thermal analysis for the organic sludge surrogate alone show primarily a broad combustion range in Figure H-4. The organic sludge surrogate was run at 1°C (1.8°F)/minute. An exothermic reaction, probably combustion of the oil (heat released and mass decreased), was present to about 400°C (752°F), at which point the heat release slope increased, suggesting the reaction mechanism changed. As evidenced by the multiple slopes and peaks, several reaction mechanisms were present during the heating process, and all resulted in a decrease of mass. The sludge is not a pure component, so the multiple peaks could indicate the reaction, the combustion, or both, of different portions of the sludge.

Previous DSC testing of Texaco Regal Oil alone in an inert atmosphere (see Figures H-5 and H-6 [Heiser 1999]) showed barely exothermic activity with one of the samples exhibiting an endothermic peak around 480°C (896°F).

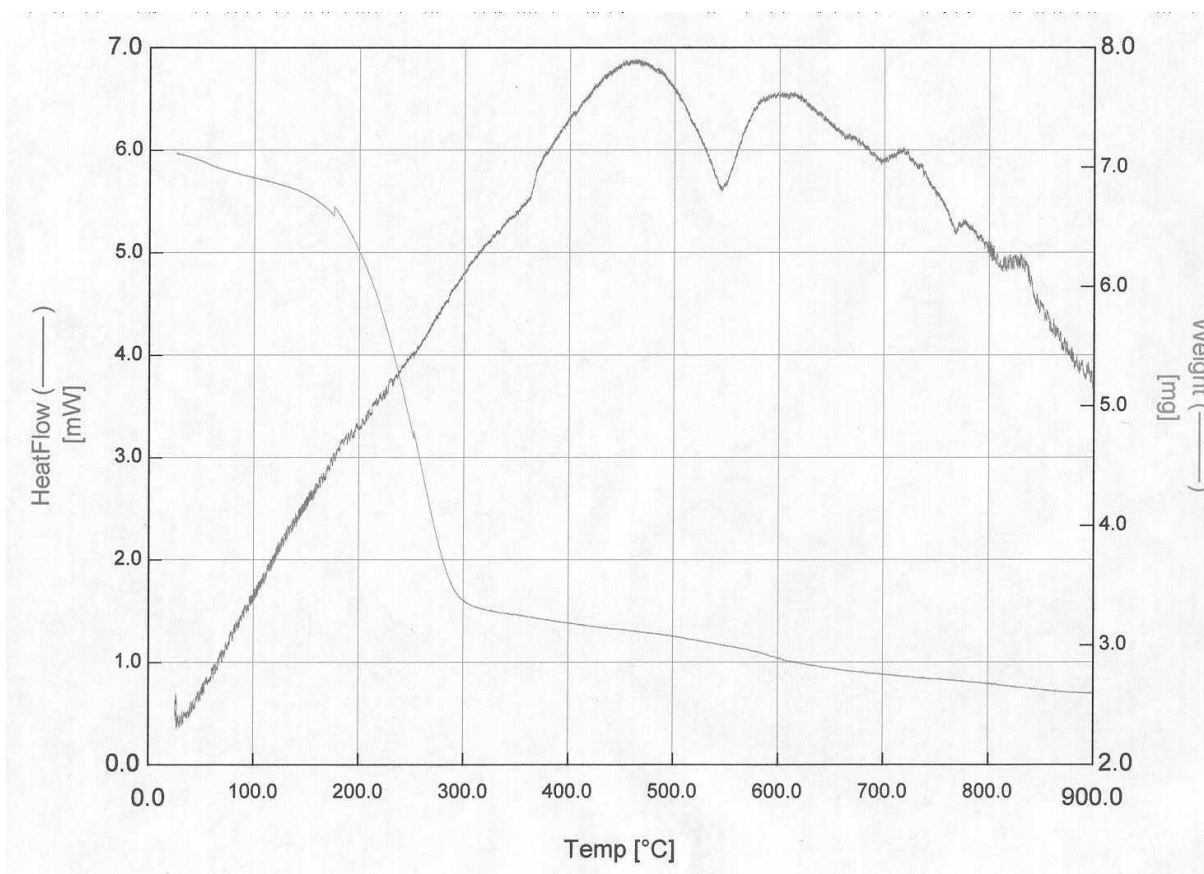


Figure H-4. Thermal gravimetric analysis of organic sludge surrogate run at 1°C (1.8°F)/minute.

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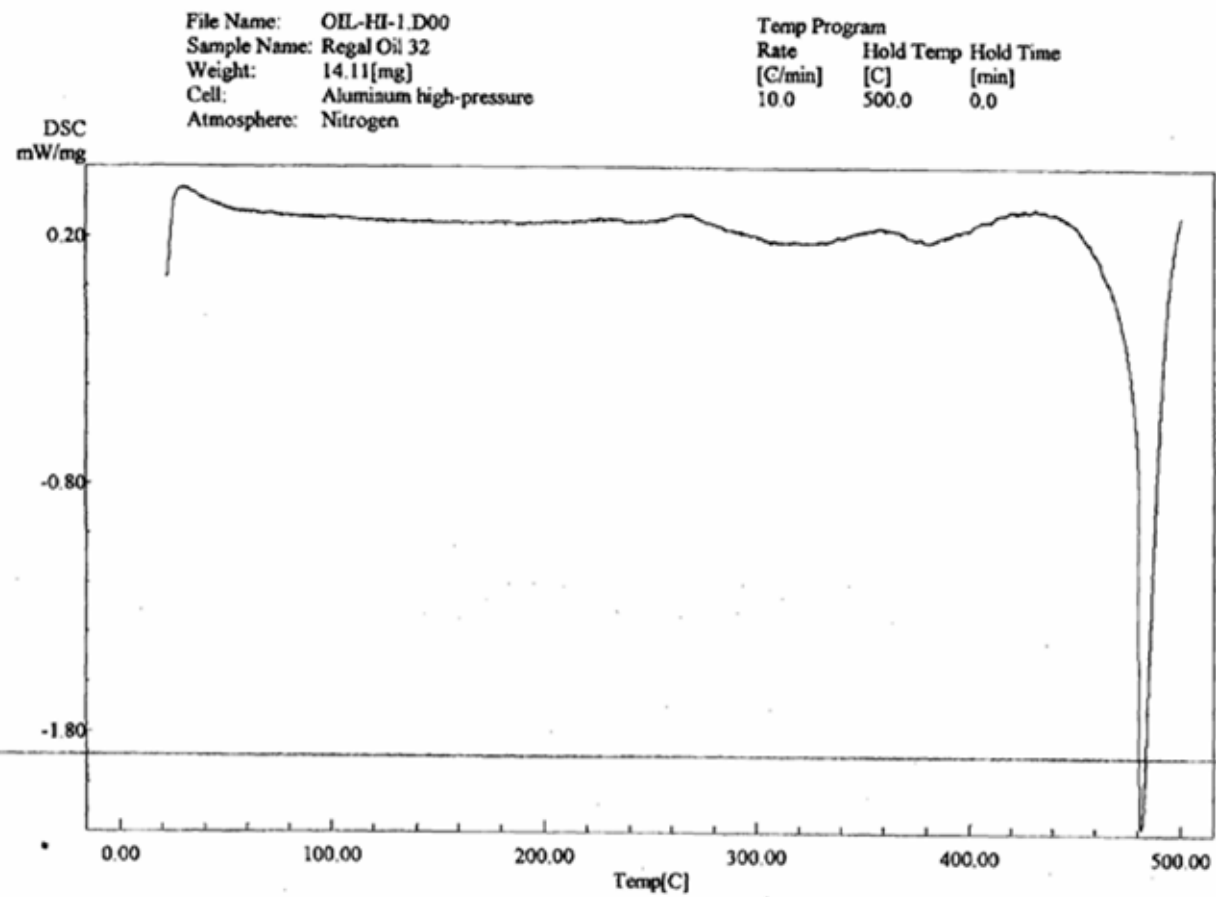


Figure H-5. Differential scanning calorimetry of oil used in organic sludge in pressurized container.

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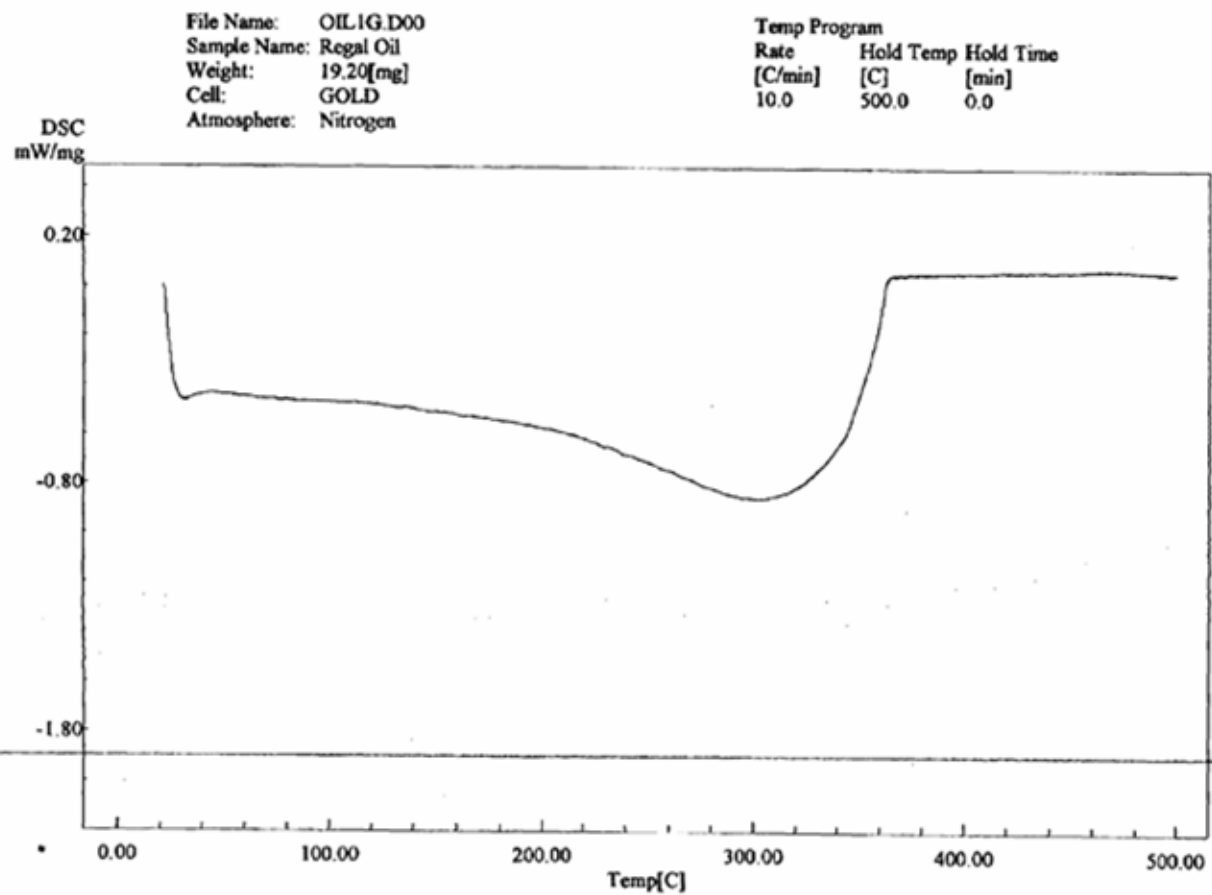


Figure H-6. Differential scanning calorimetry scan of oil used in organic sludge under inert atmosphere.

## H-5.2 Combined Waste Stream Thermo Analysis Results

Thermo analysis was run on four types of carbon (carbon powder, graphite, wax, and organic sludge) and nitrate salt sludge mixtures. With regard to nitrate salt sludge, the carbon powder was the most reactive form of carbon tested. The carbon powder simulates charred debris; the wax simulates plastics in debris, and the organic sludge is a common organic source in the waste.

The results of the nitrate salt surrogate and carbon powder mixture are discussed first. The salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the endotherm [actual or relative] in that temperature range in Figures H-7, H-8, and H-9). The rate of temperature increase in the TGA testing affects the temperature of onset, the magnitude, and the duration of the major exothermic reaction. At a heating rate of 10°C (18°F)/minute (see Figure H-7), the system remained endothermic until around 275°C (527°F); the major exothermic reaction started around 375°C (707°F) and was completed around 430°C (806°F), and a very sharp peak having a maximum heat flow of 245 mW was observed. A second, much smaller, exothermic peak was observed between 430 and 460°C (806 and 860°F) (with a mass loss of 3%). Approximately 62% of the initial sample mass was lost during the major exothermic reaction, while 3% of the initial mass was lost before the major exothermic reaction and 12% was lost after. The percent mass loss rate during the major exothermic reaction was approximately 11%/minute (62% mass loss/55°C (131°F) temperature change  $\times$  10°C (18°F)/minute heating rate = 11%/minute).

At a heating rate of 1°C (1.8°F)/minute (see Figure H-8), the system was exothermic from the start; the major exotherm (note the inflection in the heat release trace) started at approximately 350°C (662°F) and finished at approximately 425°C (797°F); a well-defined peak with a maximum heat flow of 12.4 mW was observed. The second exothermic peak was observed at 425 to 590°C (797 to 1,094°F), with a mass loss of 5%, and was more substantial than the second peak observed at the faster heating rate. Approximately 22% of the initial sample mass was lost during the major exothermic reaction, while 14% of the initial mass was lost before the major exothermic reaction, and 42% was lost after. The percent mass loss rate during the major exothermic reaction was approximately 0.29%/minute (22% mass loss/75°C (167°F) temperature change  $\times$  1°C (1.8°F)/minute heating rate = 0.29%/minute).

At a heating rate of 0.1°C (0.8°F)/minute (see Figure H-9), the system was exothermic from the start; the major exotherm (note the inflection in the heat release trace) started at approximately 275°C (527°F) and finished at approximately 360°C (680°F); a peak with a maximum heat flow of 6.8 mW was observed. The second exothermic peak was observed at 425 to 590°C (797 to 1,094°F). This peak had a maximum heat flow of 6.6 and was much broader than at higher heating rates; a mass loss of 15% was observed. Approximately 37% of the initial sample mass was lost during the major exothermic reaction, while 34% of the initial mass was lost before the major exothermic reaction, and 29% was lost and 30% was gained after. The percent mass loss rate during the major exothermic reaction was approximately 0.044%/minute (37% mass loss/85°C (185°F) temperature change  $\times$  0.1°C (0.18°F)/minute heating rate = 0.044%/minute).

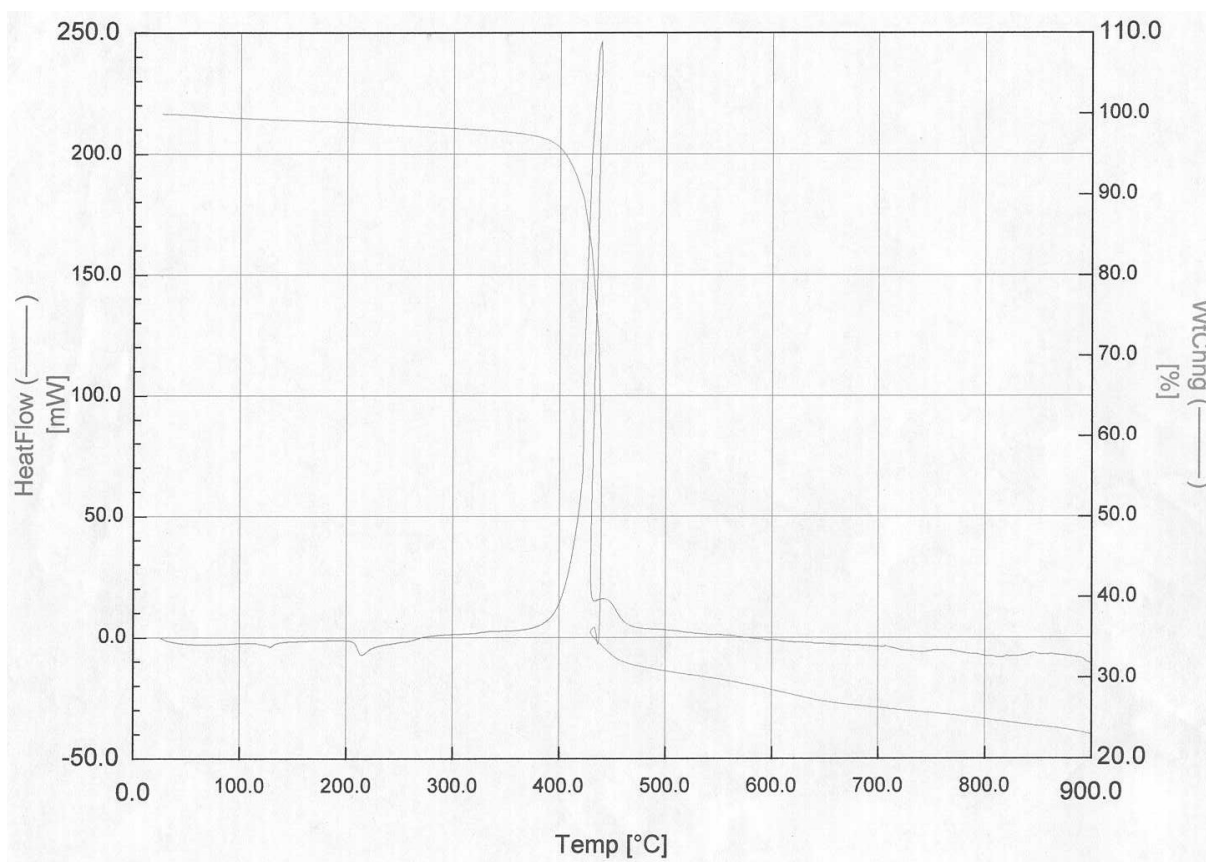


Figure H-7. Thermal gravimetric analysis of 83 wt% nitrate salt surrogate and 17 wt% carbon powder at 10°C (18°F)/minute.

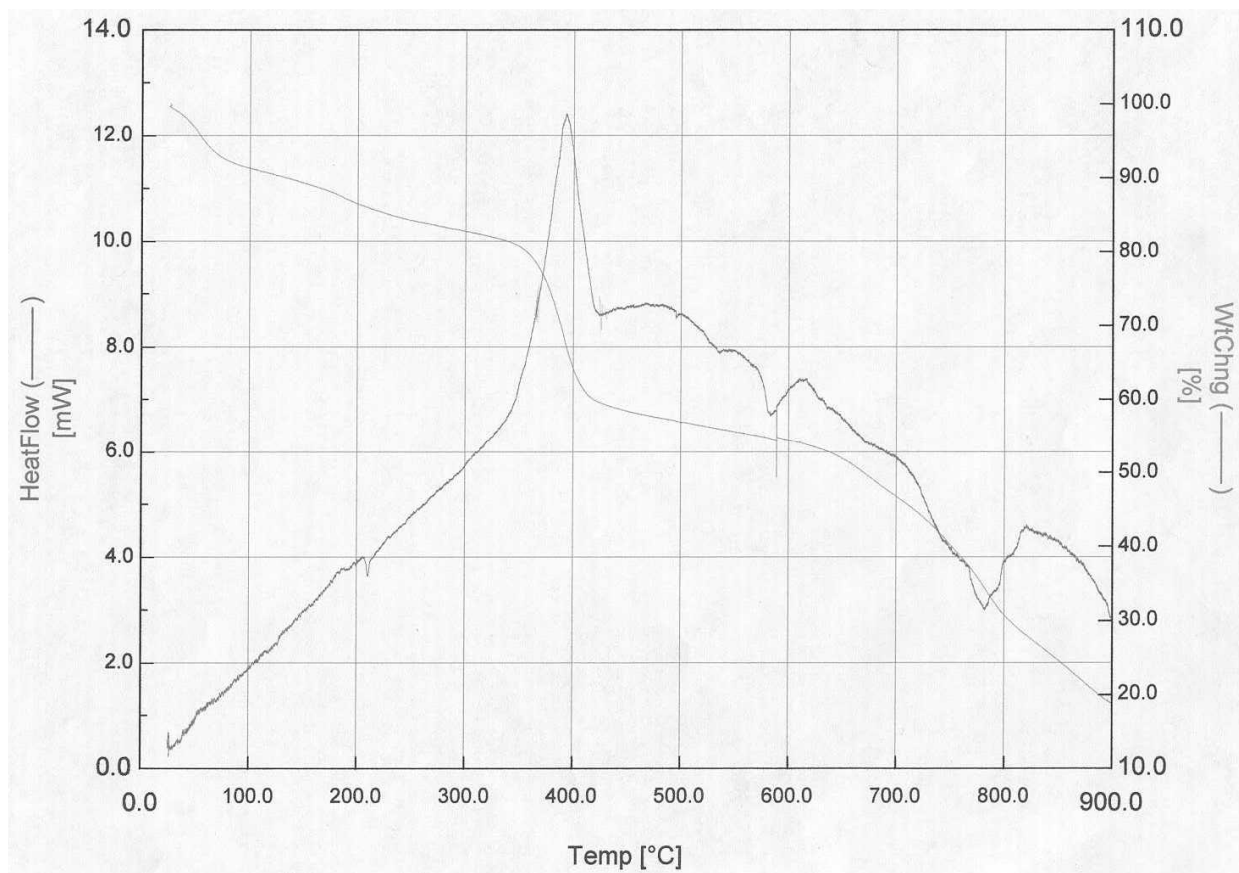


Figure H-8. Thermal gravimetric analysis of excess carbon and nitrate salt surrogate run at 1°C (1.8°F)/minute.

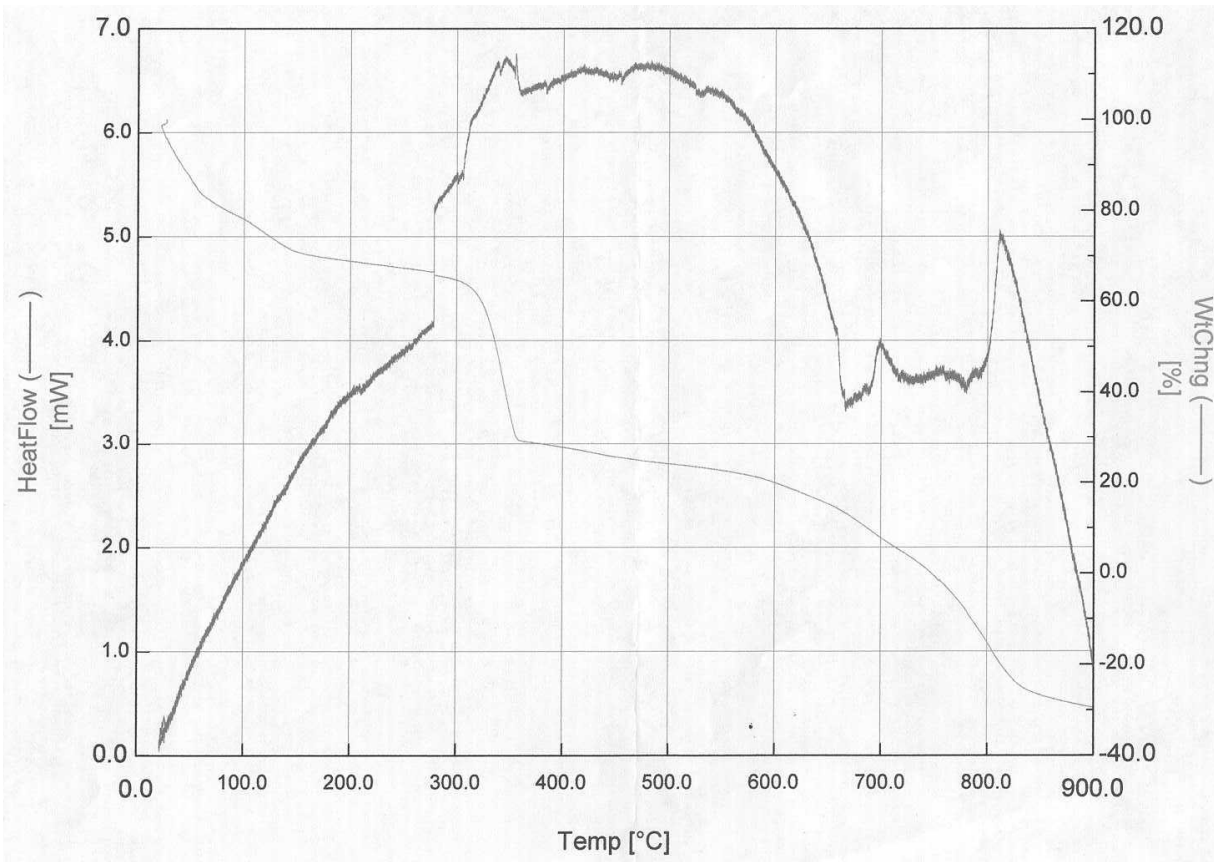


Figure H-9. Thermal gravimetric analysis of 83 wt% nitrate salt surrogate and 17 wt% carbon powder at 0.1°C (0.18°F)/minute.

Overall, as the temperature increase rate decreased:

- Peak heat flow substantially decreased
- Percent of initial mass consumed before the major exotherm increased
- Rate of percent mass loss during the major exotherm substantially decreased (see Table H-6).

Based on the relative consistency in the position and total number of peaks observed, it is expected that the same reactions were occurring at each temperature increase rate. The differences in the shapes of the curves are from the rates at which each reaction occurs. The reaction rate depends on the temperature and concentration of reactants (for first order or greater reactions). The temperature affects the intrinsic reaction rate according to Equation (H-1) (the Arrhenius equation):

$$k = Ae^{-E_a/RT} \quad (\text{H-1})$$

where:

- |                |   |                             |
|----------------|---|-----------------------------|
| k              | = | the intrinsic reaction rate |
| A              | = | a constant                  |
| E <sub>a</sub> | = | the activation energy       |

R = the ideal gas constant  
T = the absolute temperature.

The overall rate of reaction (R) is given by Equation (H-2):

$$R = k f(C) \quad (H-2)$$

where:

C = the concentration of the reactant  
f = some function depending on C.

If the temperature is increased slowly, k increases slowly, and there is more time for material to be consumed at a given temperature. The more material that is consumed before a temperature increase, the lower the overall rate R will be at a given temperature. When the temperature is increased quickly, the k and C amplify each other's affect on the overall rate, making R much faster, leading to a higher heat flow rate.

Table H-6. Summary of effects of temperature increase rate on peak heat flow, mass consumed, and rate of mass loss.

Parameter	Temperature Increase Rate		
	(10°C/minute)	(1°C/minute)	(0.1°C/minute)
Peak heat flow	245 mW	12.4 mW	6.8 mW
Percent of initial mass consumed before the major exotherm	3%	14%	34%
Rate of percent mass loss during the major exotherm	11%/minute	0.29%/minute	0.044%/minute

A DSC run (see Figure H-10 [Heiser 1999]) of a stoichiometric mixture of nitrate salt waste and graphite (87-13 mass ratio) looks quite different from the TGA run performed with a near stoichiometric mixture of nitrate salt surrogate and carbon powder (83-17 mass ratio), shown in Figure H-7. The nitrate salt waste and graphite mixture exhibits all endotherms, except for a small ( $<4.4 \text{ mW} = <0.2 \text{ mW/mg} \times 21.81 \text{ mg}$ ) relative exothermic peak around 400°C (752°F). The exothermic reaction occurs at the same temperature for both mixtures, but the magnitude of the reactions is much greater for the mixture containing carbon powder than for the mixture containing graphite. While graphite and carbon powder have the same elemental composition, C, the structure of the two forms of carbon is very different. Graphite has a definite crystal structure, while carbon powder is amorphous. The carbon in graphite is much less available for reaction than the carbon in carbon powder; this could be the reason that the reaction with carbon powder was much more exothermic than the reaction with graphite.

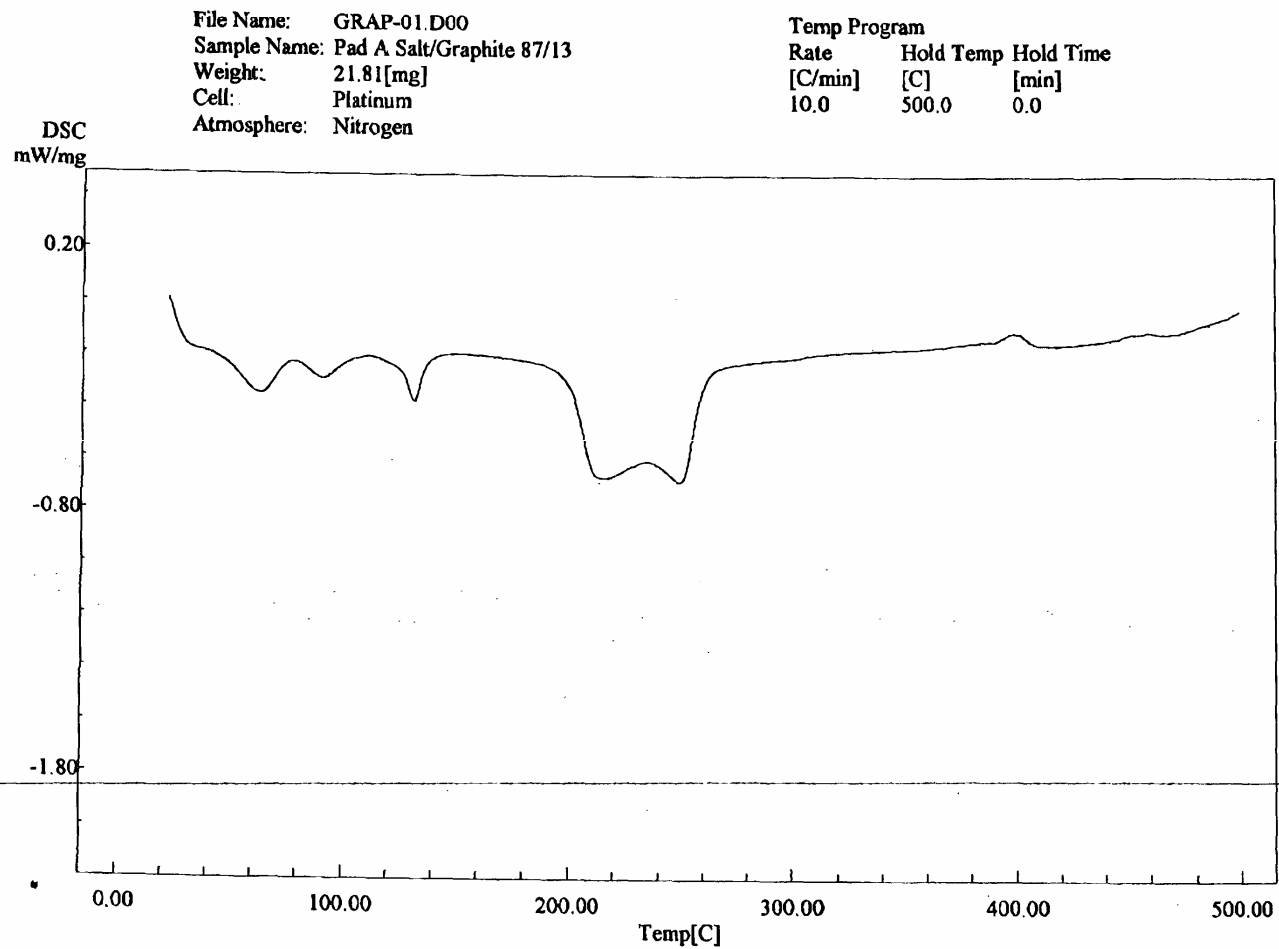


Figure H-10. Differential scanning calorimetry scan of a stoichiometric mixture of graphite and nitrate salt waste.

The reaction of nitrate salt surrogate with wax was also evaluated. As with the nitrate salt and carbon powder, the salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the endotherm) in that temperature range in Figure H-11. The rate of temperature increase in the TGA testing affects the temperature of onset, the magnitude, and the duration of the major exothermic reaction. At a heating rate of 10°C (18°F)/minute (see Figure H-11), the system remained endothermic until around 330°C (626°F), and the major exothermic reaction started around 330°C (626°F) and was completed around 520°C (968°F); a sharp peak with a maximum heat flow of 24 mW at 480°C (896°F) was observed. A second, much smaller, exothermic peak was observed between 520 and 630°C (968 and 1,166°F) (with a mass loss of 3%). Approximately 28% of the initial sample mass was lost during the major exothermic reaction, while 7% of the initial mass was lost before the major exothermic reaction, and 43% was lost after. The percent mass loss rate during the major exothermic reaction was approximately 1.5%/minute (28% mass loss/190°C (374°F) temperature change  $\times$  10°C (18°F)/minute heating rate = 1.5%/minute).

A second test was run with a temperature increase of 0.1°C (0.18°F)/minute (see Figure H-12). No endothermic region was observed before the major exotherm. The major exotherm during this run was very broad and peaked at 330°C (626°F) with a maximum heat flow of 5 mW. Mass data were not available for this run.

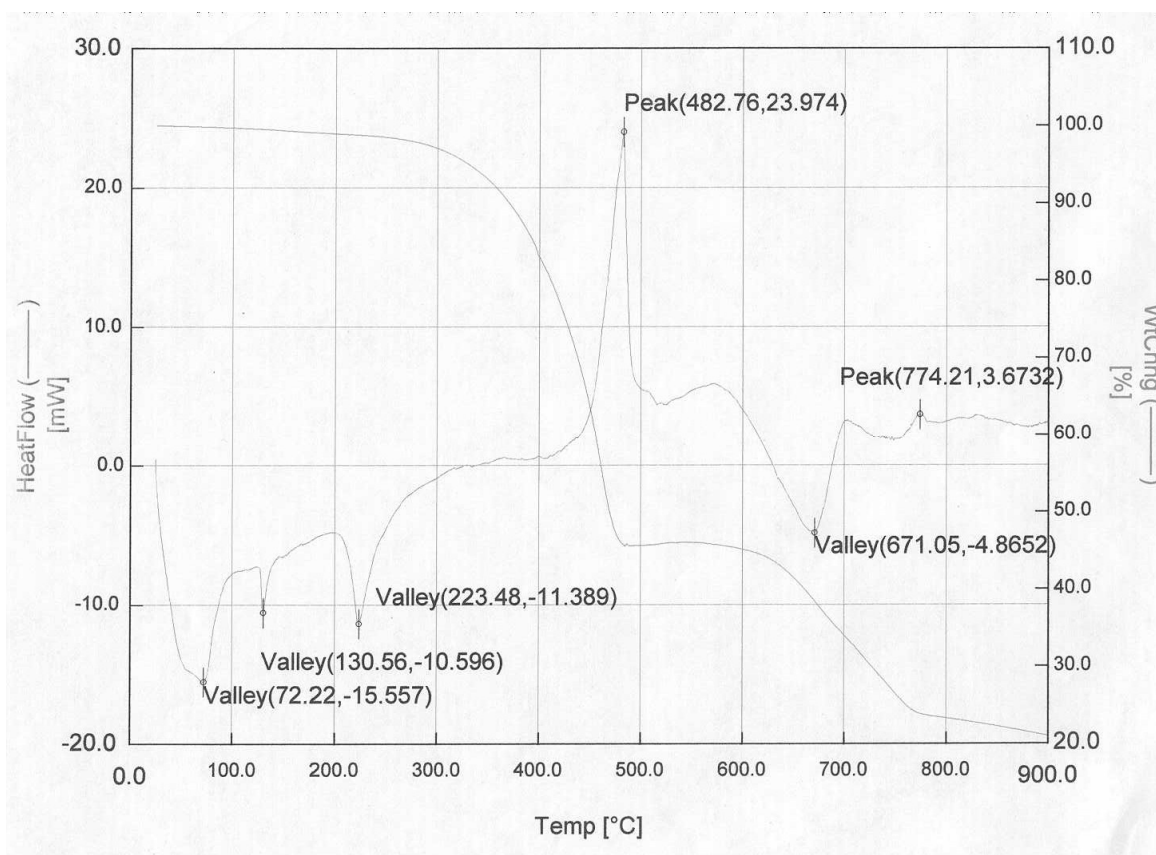


Figure H-11. Thermal gravimetric analysis of nitrate salt surrogate and wax at 10°C (18°F)/minute.

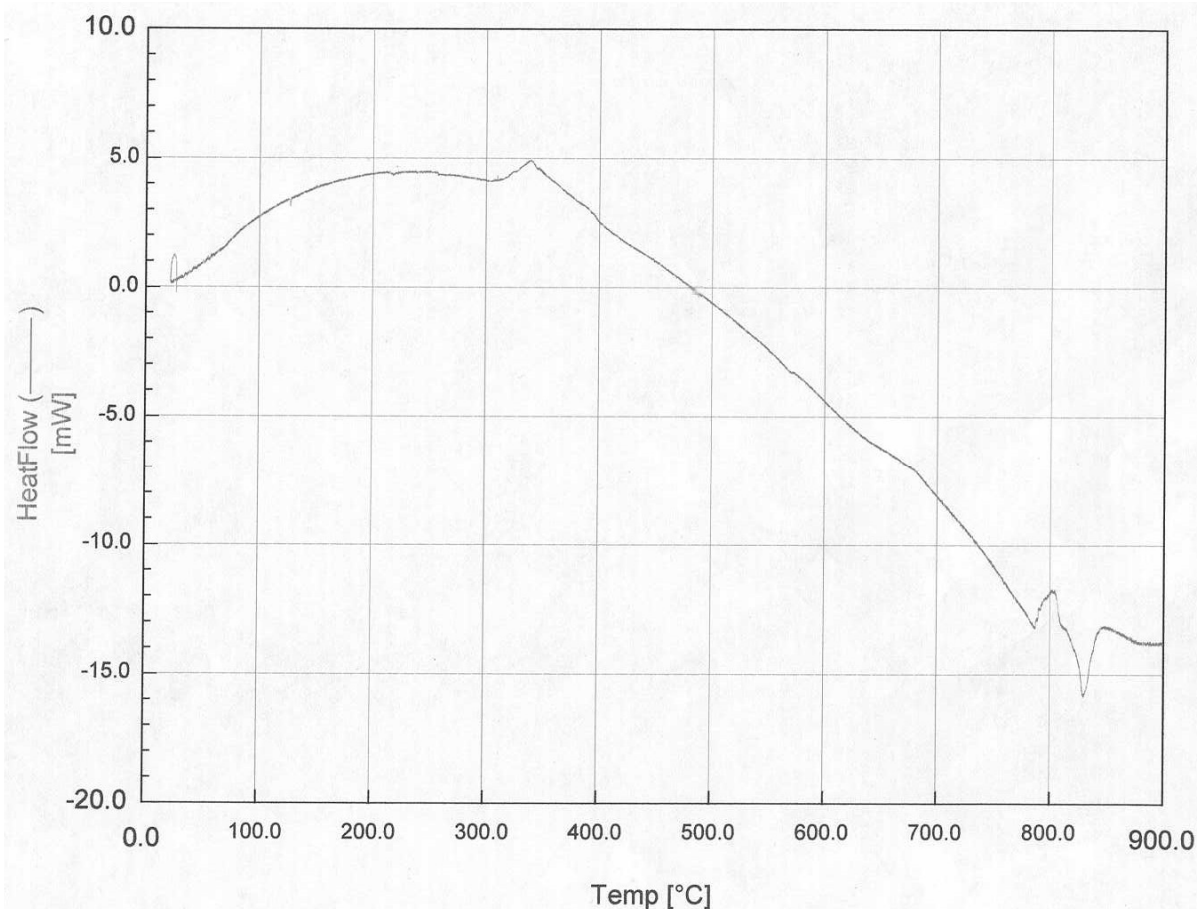


Figure H-12. Thermal gravimetric analysis of nitrate salt surrogate and wax at 0.1°C (0.18°F)/minute.

The reaction of nitrate salt surrogate with organic sludge surrogate was evaluated at a temperature increase rate of 1°C (1.8°F)/minute (see Figure H-13). The plot does not exhibit an endotherm before the major exotherm. As with the nitrate salt and carbon powder, the salts form a eutectic that melts around 212 to 220°C (413.6 to 428°F) (look for the relative endotherm) in that temperature range in Figure H-13. The major exotherm is very broad and peaks at about 380°C (716°F) with a maximum heat flow of 4.5 mW. The mass loss curve shows regions of decreased slope (slower mass loss); these regions coincide with relative endotherms. Some of the relative endotherms may be caused by vaporization of lower boiling compounds with the organic sludge surrogate. A secondary exotherm is also present and forms a broad peak. Thermo analysis 56/44 wt% mix of nitrate salt/organic sludge in Figure H-13 appears similar to both organic sludge alone in Figure H-4 and previous Brookhaven National Laboratory DSC scans of (see Figure H-14 [Heiser 1999]) the nitrate salts and oil in the sludge. The organic sludge nitrate thermo analysis shows a broad combustion area over several hours of heating. This type of combustion could be beneficial, supplementing the heat of the electrical heaters and reducing the load on the off-gas system.

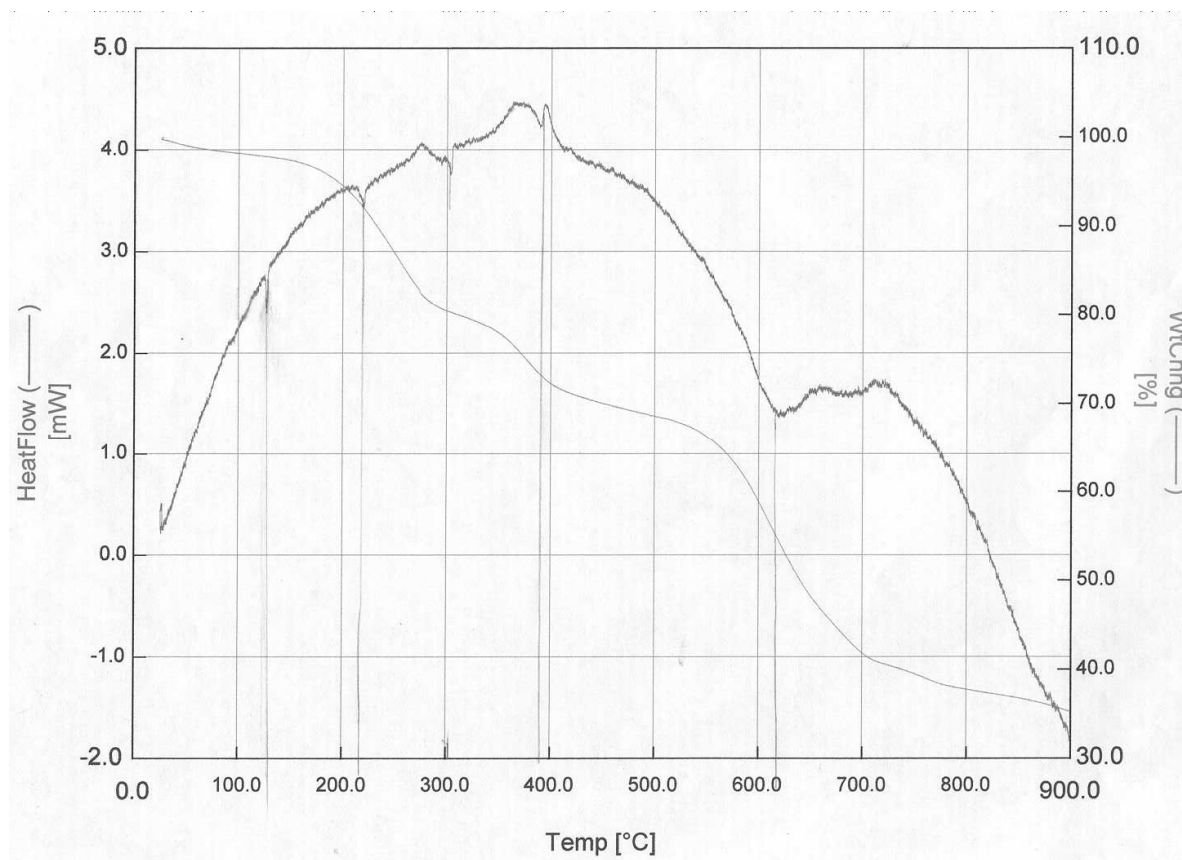


Figure H-13. Thermal gravimetric analysis of nitrate salt surrogate and organic sludge surrogate at 1°C (1.8°F)/minute.

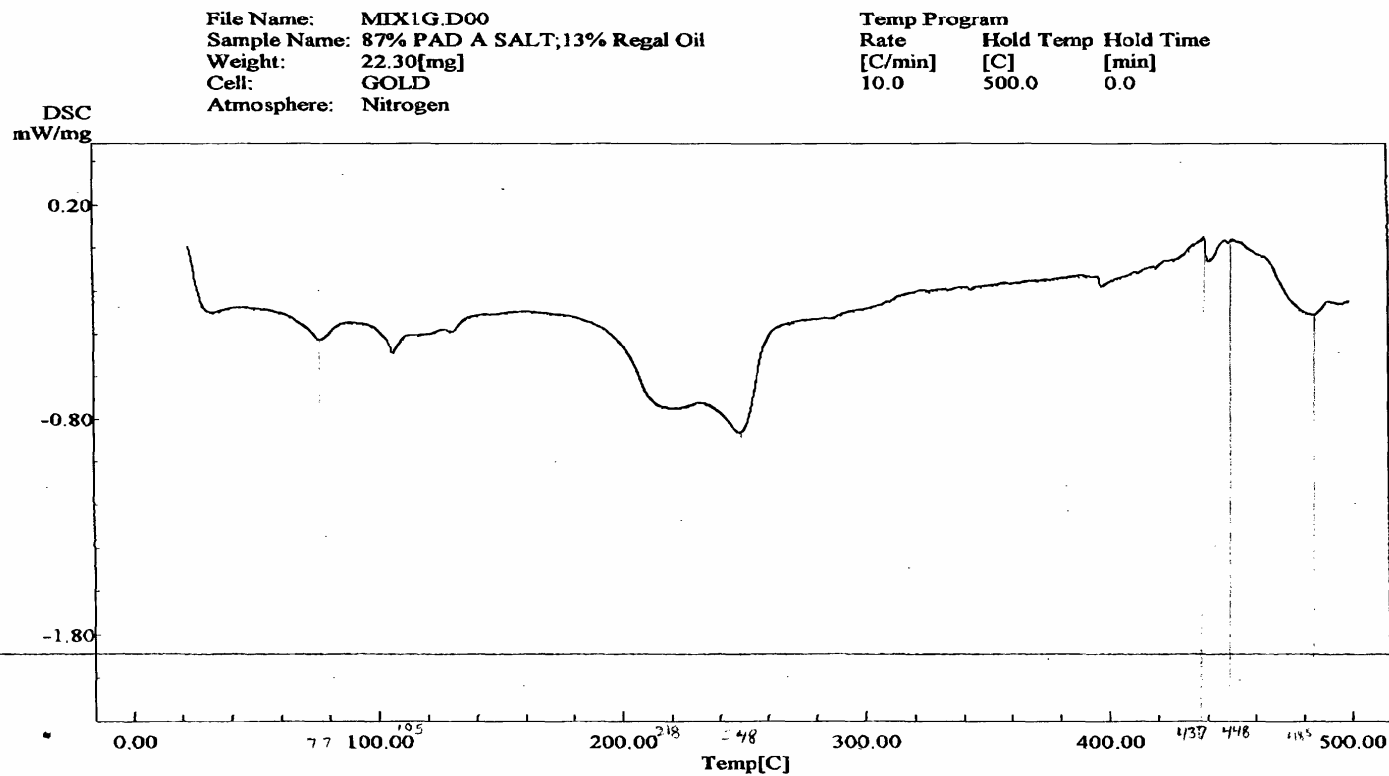


Figure H-14. Differential scanning calorimetry of organic sludge oil and nitrate salts.

The form of carbon and the rate of temperature increase affect the magnitude of nitrate salt reaction with carbon. Less structured carbon, represented by carbon power, was more reactive than more structured forms of carbon such as graphite, wax, or organic sludge. In the waste, slow charring of paper and wood could lead to carbon powderlike substances. Plastic in the waste would be expected to behave similar to the wax (both are long-chain, hydrocarbon-based materials) while graphite and organic sludge are present in the waste. Based on the data for the carbon powder and nitrate salt mixtures and the wax and nitrate salt mixtures, the rate of temperature increase may have more impact on the magnitude of the exothermic reaction than the structure of the carbon (see Figures H-7, H-8, and H-9 for carbon powder and Figures H-11 and H-12 for wax).

The salt eutectic melting point varies slightly based on the carbon source but is always well below the melting point of the major salts (308°C [586.4°F] for sodium nitrate and 334°C [633.2°F] for potassium) and the reaction temperatures. This eutectic melting point is an endotherm seen in almost all nitrate salt thermo analysis scans and is similar to previous nitrate salt DSC runs. The nitrate salt mixture in the absence of any carbon source starts to decompose endothermically beyond 500°C (932°F) and is completely decomposed before reaching 900°C (1,652°F) (see Figures H-2 and H-3). The mass change indicates the salt is decomposing. Compositional analysis after achieving this high temperature indicated nitrates were absent. Alkalinity measurements seem to indicate that some type of alkali oxide remains.

There are no major exotherms (peaks in the upward direction) in any of the single components (oil, potassium nitrate, or sodium nitrate) or single waste streams (organic sludge or nitrate salts) up to their removal before 900°C (1,652°F). There is some decomposition of the oil that indicates some combustion, but this is more a drift upward in the baseline rather than a peak. Both instrumental thermal analysis and bench-top furnace heating of the nitrate salt mixture showed weight loss (active decomposition) does not take place until 550°C (1,022°F). By the time ISTD heats the waste to the target temperature of 450°C (842°F), nitrate would be molten, but does not appear to be decomposing as rapidly as the literature decomposition temperature would indicate.

There are a few exotherms in the salt carbon waste streams for the carbon sources tested: oil, wax, or carbon powder. Reactions or decomposition occur above the melting point of the salt (212°C [413.6°F]) but below 500°C (932°F) for carbon nitrate mixtures. The TGA was taken beyond this significant mass loss point to at least 900°C (1,652°F) before the measurement was terminated. With air flow in a vacuum well, this is the expected maximum temperature of the borehole wall in the ISTD field system.

The heating element itself may exceed 1,000°C (1,832°F), but generally, waste and soil temperatures are well below this because of the low flow of extraction air and heat conduction losses. Few, if any, nonvolatile organics can exist at heater temperatures with any oxygen around. A very small amount of solid waste actually contacts the outer slotted casing, being limited to the surface area of the heater. For an extended multimonth run, the borehole wall temperature may extend into the soil several inches, sintering soil and forming a reactive surface somewhat like a fluidized bed (Vinegar, Stegemeier, and Sheldon 1997).

Thermal analysis was performed on three carbon-containing waste surrogates: organic sludge, wax, and carbon powder mixed with the nitrate salt surrogate. Reactions at high heat rates were observed with the carbon powder and wax and were significantly reduced as ISTD heating rates were approached. Organic sludge does not react with nitrate salts beyond a normal combustion when heated in air. Oil in organic sludge is substantially removed before the range where most nitrate-carbon reactions occur.

The 0.9% organic and 0.3% nitrites within the salts themselves are insufficient to cause extensive reactivity.

For the nitrate salt, waters-of-hydration and crystallization shifts give small endotherms, but melting gives the largest endotherm. The melting point of the salt mixture is 80 to 100°C (176 to 212°F) lower than the individual alkali nitrate melting points because of the formation of a eutectic. Auto decomposition of salts seems to occur primarily above 500°C (932°F). Decomposition of the salts alone is very slow at the target temperature of 450°C (842°F).

The chlorinated solvents in the sludge vaporize with the water at atmospheric pressure even before reaching the temperature of the highest boiling point solvent (tetrachloroethene at 120°C [248°F]).

The oil in the sludge reacts with air incompletely, leaving a small amount of tar that can react with the nitrate salts in a similar fashion as normal combustion.

Table H-7. Weight loss when heating organic sludge and nitrate salt waste surrogates.

Waste Surrogate	Heating Method	Test Temperature		
		105°C (cumulative wt%)	275°C (cumulative wt%)	450°C (cumulative wt%)
Nitrate salt	TGA <sup>a</sup>	0.5 <sup>c</sup>	1.4	3
Nitrate salt	Furnace <sup>b</sup>	0.2 <sup>c</sup>	1.8	4
Organic sludge	TGA <sup>a</sup>	20 <sup>d</sup>	50	54
Organic sludge	Furnace <sup>b</sup>	43	58	68
Organic sludge and nitrate salt	TGA <sup>a</sup>	10	19	32
Organic sludge and nitrate salt	Furnace <sup>b</sup>	13	17	34

a. TGA run at 1°C/minute

b. Furnace is run at 24 hours per temperature increment, which averages to a heat rate of about 0.1°C/minute over the entire 450°C range

c. Water loss

d. Because of the small sample size and time before analysis, the sample in the alumina crucible had probably lost much of the chlorinated organic solvent originally in the surrogate before heating began.

TGA = thermal gravimetric analysis

## H-6. REFERENCES

ASTM E537-02, 2002, "Standard Test Method for The Thermal Stability Of Chemicals By Differential Scanning Calorimetry," ASTM International.

Clements, Thomas L., Jr. and D. E. Kudera, 1985, *TRU Waste Sampling Program: Volume I-Waste Characterization*, EGG-WM-6503, Idaho National Engineering Laboratory.

CRC, 2000, *Handbook of Chemistry and Physics*, Boca Raton: Chemical Rubber Company Press.

Dick, John R., 2001, *Nitrate Explosives Tests to Support the Operable Unit 7-13/14 In Situ Vitrification Project*, INEEL/EXT-01-00265, Rev. 0, Idaho National Engineering and Environmental Laboratory.

DOE-ID, 2004, *Remedial Action Report for the OU 7-10 Glovebox Excavator Method Project*, DOE/NE-ID-11155, Rev. 0, U.S. Department of Energy Idaho Operations Office.

- Heiser, J. H., 1999, *Thermal Analysis of INEEL Pad-A Salt Waste Using Differential Scanning Calorimetry*, Brookhaven National Laboratory.
- Reid, R. C., J. M. Prausnitz, and B. E. Poling, 1987, *Properties of Gases and Liquids*, New York: McGraw-Hill.
- Shaw, P. G., 1999, *Nitrate Organic Reactivity Differential Scanning Calorimetry Results*, Brookhaven National Laboratory.
- Shaw, Peter, Brenda Anderson, and Douglas Davis, 1993, *Laboratory Scale Vittrification of Low-Level Radioactive Nitrate Salts and Soils from the Idaho National Engineering Laboratory*, EGG-WTD-10640, Idaho National Engineering Laboratory.
- Vinegar, H. J., G. L. Stegemeier, and R. B. Sheldon, 1997, "Remediation of Deep Soil Using Thermal Vacuum Wells," *Society of Petroleum Engineers Annual Technical Conference, San Antonio, Texas, October 1997*, pp. 905–918.
- Yancey, Neal A., Peter G. Shaw, David F. Nickelson, Gretchen E. Matthern, and Guy G. Loomis, 2003, *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14*, INEEL/EXT-03-00059, Rev. 0, Idaho National Engineering and Environmental Laboratory, Idaho Completion Project.

